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<b>(54) Title:</b> CONTINUOUS PROCESS FOR PRODUCING ANIONIC CLAY		
<b>(57) Abstract</b>  <p>This patent describes an economical and environment-friendly continuous process for the synthesis of anionic clays with carbonate and/or hydroxide anions as the charge-balancing interlayer species. It involves reacting a slurry comprising aluminium trihydrate and/or its calcined form, with a magnesium source. There is no necessity to wash or filter the product. It can be spray dried directly to form microspheres or can be extruded to form shaped bodies. The product can be combined with other ingredients in the manufacture of catalysts, absorbents, pharmaceuticals, cosmetics, detergents, and other commodity products.</p>		

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## CONTINUOUS PROCESS FOR PRODUCING ANIONIC CLAY

## BACKGROUND OF THE INVENTION

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This invention involves the continuous preparation of anionic clays and the preparation of Mg-Al solid solutions by heat-treatment of the anionic clay. Anionic clays have a crystal structure which consists of positively charged layers built up of specific combinations of metal hydroxides between which there are anions and water molecules. Hydrotalcite is an example of a naturally occurring anionic clay, in which carbonate is the predominant anion present. Meixnerite is an anionic clay wherein hydroxyl is the predominant anion present.

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15 In hydrotalcite-like anionic clays the brucite-like main layers are built up of octahedra alternating with interlayers in which water molecules and anions, more particularly carbonate ions, are distributed. The interlayers may contain anions such as  $\text{NO}_3^-$ ,  $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{SiO}_3^{2-}$ ,  $\text{CrO}_4^{2-}$ ,  $\text{BO}_3^{2-}$ ,  $\text{MnO}_4^-$ ,  $\text{HGao}_3^{2-}$ ,  $\text{HVO}_4^{2-}$ ,  $\text{ClO}_4^-$ ,  $\text{BO}_3^{2-}$ , pillaring anions such as  $\text{V}_{10}\text{O}_{28}^{6-}$  and  $\text{Mo}_7\text{O}_{24}^{6-}$ ,  
20 monocarboxylates such as acetate, dicarboxylates such as oxalate, alkyl sulphonates such as laurylsulphonate.

It should be noted that a variety of terms are used to describe the material which is referred to in this patent as an anionic clay. Hydrotalcite-like and layered double hydroxide are interchangeably used by those skilled in the art. In this patent application we refer to the materials as anionic clays, comprising within that term hydrotalcite-like and layered double hydroxide materials.

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The preparation of anionic clays has been described in many prior art publications.

30

Recently, two major reviews of anionic clay chemistry were published in which

the synthesis methods available for anionic clay synthesis have been summarized, F. Cavani et al "Hydrotalcite-type anionic clays: Preparation, Properties and Applications," Catalysis Today, 11 (1991) Elsevier Science Publishers B. V. Amsterdam.

- 5 J P Besse and others "Anionic clays:trends in pillary chemistry, its synthesis and microporous solids"(1992), 2, 108, editors: M.I. Occelli, H.E. Robson, Van Nostrand Reinhold, N.Y.

In these reviews the authors state that a characteristic of anionic clays is that  
10 mild calcination at 500 °C results in the formation of a disordered MgO-like product. Said disordered MgO-like product is distinguishable from spinel (which results upon severe calcination) and from anionic clays. In this patent application we refer to said disordered MgO-like materials as Mg-Al solid solutions. Furthermore, these Mg-Al solid solutions contain a well-known  
15 memory effect whereby the exposure to water of such calcined materials results in the reformation of the anionic clay structure.

For work on anionic clays, reference is given to the following articles:

- Helv. Chim. Acta, 25, 106-137 and 555-569 (1942)  
20 J. Am. Ceram. Soc., 42, no. 3, 121 (1959)  
Chemistry Letters (Japan), 843 (1973)  
Clays and Clay Minerals, 23, 369 (1975)  
Clays and Clay Minerals, 28, 50 (1980)  
Clays and Clay Minerals, 34, 507 (1996)  
25 Materials Chemistry and Physics, 14, 569 (1986).

In addition there is an extensive amount of patent literature on the use of anionic clays and processes for their preparation.

European Patent Application 0 536 879 describes a method for introducing pH-  
30 dependent anions into the clay. The clay is prepared by the addition of a

solution of  $\text{Al}(\text{NO}_3)_3$  and  $\text{Mg}(\text{NO}_3)_2$  to a basic solution containing borate anions. The product is then filtered, washed repeatedly with water, and dried overnight. Additionally mixtures of Zn/Mg are used.

- 5 In US 3,796,792 by Miyata entitled "Composite Metal Hydroxides" a range of materials is prepared into which an extensive range of cations is incorporated, including Sc, La, Th, In, etc. In the examples given solutions of the divalent and trivalent cations are prepared and mixed with base to cause co-precipitation. The resulting products are filtered, washed with water, and dried at 80 °C.
- 10 Example 1 refers to Mg and Al and Example 2 to Mg and Bi. Other examples are given, and in each case soluble salts are used to make solutions prior to precipitation of the anionic clay at high pH.

In US 3,879,523 by Miyata entitled "Composite Metal Hydroxides" also a large  
15 number of preparation examples is outlined. The underlying chemistry, however, is again based on the co-precipitation of soluble salts followed by washing and drying. It is important to emphasize that washing is a necessary part of such preparations, because to create a basic environment for co-precipitation of the metal ions a basic solution is needed and this is provided by  
20  $\text{NaOH}/\text{Na}_2\text{CO}_3$  solutions. Residual sodium, for example, can have a significant deleterious effect on the subsequent performance of the product as a catalyst or oxide support.

In US 3879525 (Miyata) very similar procedures are again described.  
25

In US 4,351,814 to Miyata et al. a method for making fibrous hydrotalcite is described. Such materials differ in structure from the normal plate-like morphology. The synthesis again involves soluble salts. For example, an aqueous solution of a mixture of  $\text{MgCl}_2$  and  $\text{CaCl}_2$  is prepared and suitably  
30 aged. From this a needle-like product  $\text{Mg}_2(\text{OH})_3\text{Cl}\cdot 4\text{H}_2\text{O}$  precipitates. A separate

solution of sodium aluminate is then reacted in an autoclave with the solid  $\text{Mg}_2(\text{OH})_3\text{Cl}\cdot 4\text{H}_2\text{O}$  and the product is again filtered, washed with water, and dried.

- 5 In US 4,458,026 to Reichle, in which heat-treated anionic clays are described as catalysts for aldol condensation reactions, again use is made of magnesium and aluminium nitrate salt solutions. Such solutions being added to a second solution of  $\text{NaOH}$  and  $\text{Na}_2\text{CO}_3$ . After precipitation the slurry is filtered and washed twice with distilled water before drying at  $125^\circ\text{C}$ .

10

In US 4,656,156 to Misra the preparation of a novel absorbent based on mixing activated alumina and hydrotalcite is described. The hydrotalcite is made by reacting activated  $\text{MgO}$  (prepared by activating a magnesium compound such as magnesium carbonate or magnesium hydroxide) with aqueous solutions containing aluminate, carbonate and hydroxyl ions. As an example the solution is made from  $\text{NaOH}$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{Al}_2\text{O}_3$ . In particular, the synthesis involves the use of industrial Bayer liquor as the source of  $\text{Al}$ . The resulting products are washed and filtered before drying at  $105^\circ\text{C}$ .

20

In US 4,904,457 to Misra a method is described for producing hydrotalcites in high yield by reacting activated magnesia with an aqueous solution containing aluminate, carbonate, and hydroxyl ions.

- 25 The methodology is repeated in US 4,656,156.

In US 5,507,980 to Kelkar et al. a process is described for making novel catalysts, catalyst supports, and absorbers comprising synthetic hydrotalcite-like binders. The synthesis of the typical sheet hydrotalcite involves reacting pseudo-boehmite to which acetic acid has been added to peptize the pseudo-

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boehmite. This is then mixed with magnesia. More importantly, the patent summary states clearly that the invention uses mono carboxylic organic acids such as formic, propionic and isobutyric acid. In this patent the conventional approaches to preparing hydrotalcite are presented.

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In US 5,439,861 a process is disclosed for preparing a catalysts for synthesis gas production based on hydrotalcite. The method of preparation is again based, on the co-precipitation of soluble salts by mixing with base, for example, by the addition of a solution of  $\text{RhCl}_3$ ,  $\text{Mg}(\text{NO}_3)_2$  and  $\text{Al}(\text{NO}_3)_3$  to a solution of  $\text{Na}_2\text{CO}_3$  and  $\text{NaOH}$ .

10

Also in US 5,399,537 to Bhattacharyya in the preparation of nickel-containing catalysts based on hydrotalcite use is made of the co-precipitation of soluble magnesium and aluminium salts.

15

In US 5,591,418 to Bhattacharyya a catalyst for removing sulphur oxides or nitrogen oxides from a gaseous mixture is made by calcining an anionic clay, said anionic clay having been prepared by co-precipitation of a solution of  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{Al}(\text{NO}_3)_3$  and  $\text{Ce}(\text{NO}_3)_3$ . The product again is filtered and repeatedly washed with de-ionized water.

20

In US 5,114,898/WO 9110505 Pinnavaia et al. describe layered double hydroxide sorbents for the removal of sulphur oxide(s) from flue gases, which layered double hydroxide is prepared by reacting a solution of Al and Mg nitrates or chlorides with a solution of  $\text{NaOH}$  and  $\text{Na}_2\text{CO}_3$ . In US 5,079,203 /WO 9118670 layered double hydroxides intercalated with polyoxo anions are described, with the parent clay being made by co-precipitation techniques.

25

In US 5,578,286 in the name of Alcoa a process for the preparation of meixnerite is described. Said meixnerite may be contacted with a dicarboxylate

30

or polycarboxylate anion to form a hydrotalcite-like material. In comparative examples 1-3 hydromagnesite is contacted with aluminium trihydrate in a CO<sub>2</sub> atmosphere, greater than 30 atmospheres. No hydrotalcite was obtained in these examples.

5

In US 5,514,316 a method for the preparation of meixnerite is described using magnesium oxide and transition alumina. For comparative purposes aluminium trihydrate was used in combination with magnesium oxide. It was indicated that this method did not work as well as with transition alumina.

10

US 4,454,244 and US 4,843,168 describe the use of pillaring anions in anionic clays.

15

In US 4,946,581 and US 4,952,382 to van Broekhoven co-precipitation of soluble salts such as Mg(NO<sub>3</sub>)<sub>2</sub> and Al(NO<sub>3</sub>)<sub>3</sub> with, and without the incorporation of rare earth salts was used for the preparation of anionic clays as catalyst components and additives. A variety of anions and di- and tri-valent cations are described.

20

As indicated in the description of the prior art given-above, there are many applications of anionic clays.

These include but are not restricted to: catalysts, adsorbents, drilling muds, catalyst supports and carriers, extenders and applications in the medical field. In particular van Broekhoven has described their use in SO<sub>x</sub> abatement

25

chemistry.

Because of this wide variety of large-scale commercial applications for these materials, new processes utilizing alternative inexpensive raw materials and which can be carried out in continuous mode are needed to provide a more  
30 cost-effective and environmentally compatible processes for making anionic



clays. In particular, from the prior art described above one can conclude that the preparation process can be improved in the following ways: the use of cheaper sources of reactants, processes for easier handling of the reactants, so that there is no need for washing or filtration, eliminating the filtration problems associated with these fine-particled materials, the avoidance of alkali metals (which can be particularly disadvantageous for certain catalytic applications): In prior art preparations organic acids were used to peptize alumina. The use of organic acids is expensive and introduces an additional step in the synthesis process and is therefore not cost-effective. Further, in drying or calcining the anionic clay prepared by prior art processes gaseous emissions of nitrogen oxides, halogens, sulphur oxides, etc. are encountered which cause environmental pollution problems. Moreover, none of the preparation methods described in the prior art provide continuous processes for the preparation of anionic clays.

15

#### SUMMARY OF THE INVENTION

Our invention includes a process for producing anionic clays using raw materials which are inexpensive and utilizing such raw materials in a simple process which is extremely suitable to be carried out in continuous mode. Said process involves reacting mixtures with or without stirring in water at ambient or elevated temperature at atmospheric or elevated pressure. Such continuous processes can be operated in standard industrial equipment. More specifically, there is no need for washing or filtering, and a wide range of ratios of Mg/Al in the reaction product is possible.

In the continuous process according to the invention an aluminium source and a magnesium source, for instance magnesium oxide or brucite, are fed to a reactor and reacted in aqueous suspension to obtain an anionic clay. This invention involves the use of alumina trihydrate (such as gibbsite, bayerite or

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nordstrandite) or thermally treated forms thereof as aluminium source. The reaction is carried out at ambient or elevated temperature and ambient or elevated pressure and the reaction mixture results in the direct formation of an anionic clay which can be obtained by simply drying the slurry continuously  
5 retrieved from the reactor. The powder X-ray diffraction pattern (PXRD) suggests that the product is comparable to anionic clays made by other standard (batch) methods. The physical and chemical properties of the product are also comparable to those anionic clays made by the other conventional methods. The overall process of this invention is very flexible, enabling a wide  
10 variety of anionic clay compositions and anionic clay-like materials involving for example carbonate, hydroxide and other anions to be prepared in an economically and environmental-friendly manner.

#### 15 BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a PXRD pattern of commercially available Mg-Al carbonate anionic clay.

Figure 2 shows a PXRD pattern of a Mg-Al carbonate anionic clay prepared by  
20 coprecipitation.

#### DETAILED DESCRIPTION OF THE INVENTION

This invention involves the continuous preparation of anionic clays. In particular  
25 it describes a process for the preparation of an anionic clay wherein an aluminium source and a Magnesium source are fed to a reactor and reacted in aqueous suspension to obtain an anionic clay, the aluminium source being aluminium trihydrate or its thermally treated forms. Said magnesium source may be composed of a solution of a magnesium salt, a solid magnesium-  
30 bearing compound or a mixture of the two. Reaction between the Mg source

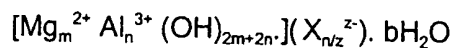
and aluminium trihydrate or its thermally treated form results in the direct formation of an anionic clay. Said reaction takes place at room temperature or higher. At temperatures higher than 100 °C, the reaction is preferably carried out under autogeneous conditions. In the method according to the invention  
5 carbonate, hydroxyl, or other anions or mixtures thereof, either provided within the reaction medium for example by feeding a soluble salt to the reactor or absorbed during the synthesis from the atmosphere, are incorporated into the interlayer region as the necessary charge-balancing anion.

10 Anionic clays prepared by this method exhibit the well known properties and characteristics (e.g. chemical analysis, powder X-ray diffraction pattern, FTIR, thermal decomposition characteristics, surface area, pore volume, and pore size distribution) usually associated with anionic clays prepared by the customary and previously disclosed methods.

15 Upon being heated, anionic clays generally form Mg-Al solid solutions, and at higher temperatures, spinels. When used as a catalyst, an adsorbent (for instance a SO<sub>x</sub> adsorbent for catalytic cracking reactions), or a catalyst support, the anionic clay according to the invention is usually heated during preparation  
20 and is thus in the Mg-Al solid solution form. During use in a FCC unit, the catalyst or adsorbent is converted from an anionic clay into Mg-Al solid solutions.

Therefore, the present invention is also directed to a process wherein an  
25 anionic clay prepared by the continuous process according to the invention, is heat-treated at a temperature between 300 and 1200 °C to form a Mg-Al-containing solid solution and/or spinel.

The anionic clay according to the invention has a layered structure  
30 corresponding to the general formula



- Wherein m and n have a value such that m/n=1 to 10, preferably 1 to 6, and b has a value in the range of from 0 to 10, generally a value of 2 to 6 and often a value of about 4. X may be  $\text{CO}_3^{2-}$ ,  $\text{OH}^-$  or any other anion normally present in the interlayers of anionic clays. It is more preferred that m/n should have a value of 2 to 4, more particularly a value close to 3.
- 10 Since the continuous process disclosed in this patent does not require washing of the product or filtering, there is no filtrate waste or gaseous emissions (e.g. from acid decomposition), making the process particularly environmental-friendly and more suited to the environmental constraints which are increasingly imposed on commercial operations. The product can be spray dried directly to form microspheres or can be extruded to form shaped bodies.

#### Aluminium source

- The present invention includes the use of crystalline aluminium trihydrate (ATH), for example gibbsite provided by Reynolds Aluminium Company RH-20® or JM Huber Micral ® grades. Also BOC (Bauxite Ore Concentrate), bayerite and nordstrandite are suitable aluminium trihydrates. BOC is the cheapest alumina source. The alumina trihydrate is preferred to have a small particle size. In another embodiment of the invention thermally treated forms of gibbsite are used. Combinations of aluminium trihydrate and thermally treated forms of aluminium trihydrate can also be used. The calcined aluminium trihydrate is readily obtained by thermally treating aluminium trihydrate (gibbsite) at a temperature ranging from 100 to 800 °C for 15 minutes to 24 hours. In any event, the calcining temperature and time for obtaining calcined aluminium trihydrate should be sufficient to cause a measurable increase of the

surface area in view of the surface area of the gibbsite as produced by the Bayer process which is generally between 30 and 50 m<sup>2</sup>/g. It should be noted that within the concept of this invention flash calcined alumina is also considered to be a thermally treated form of aluminium trihydrate, although generally it is considered a totally different alumina. Flash calcined alumina is obtained by treating aluminium trihydrate at temperatures between 800-1000 °C for very short periods of time in special industrial equipment, as is described in US 4,051,072 and US 3,222,129. Combinations of various thermally treated forms of aluminium trihydrate can also be used. Preferably the aluminium source is fed to the reactor in the form of a slurry. In particular we emphasize that there is no need to use a peptizable alumina source (gibbsite is not peptizable) and as a result no need to add either mineral or organic acid to vary the pH of the mixture. In the process according to our invention other aluminium sources beside aluminium trihydrate or its thermally treated forms may be fed to the reactor such as oxides and hydroxides of aluminium, (e.g. sols, flash calcined alumina, gels, pseudo-boehmite, boehmite) aluminium salts such as aluminium nitrate, aluminium chloride, aluminium chlorohydrate and sodium aluminate. Said other aluminium sources may be soluble or insoluble in water and may be added to the aluminium trihydrate and/or its thermally treated form or it may be fed to the reactor separately as a solid, a solution or as a suspension.

#### Magnesium source

Mg-bearing sources which may be used include MgO, Mg(OH)<sub>2</sub>, magnesium acetate, magnesium formate, magnesium hydroxy acetate, hydromagnesite (Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>), magnesium carbonate, magnesium bicarbonate, magnesium nitrate, magnesium chloride, dolomite and sepiolite. Both solid Mg sources and soluble Mg salts are suitable. Also combinations of Mg sources may be used. The magnesium source may be fed to the reactor as a solid, a solution, or,

preferably, as a slurry. The magnesium source may also be combined with the aluminium source before it is fed to the reactor.

### Conditions

5

Because of its simplicity, this process is particularly suitable to be carried out in a continuous mode. Thereto an aluminium source and a magnesium source are fed to a reactor and reacted in aqueous suspension to obtain an anionic clay.

10 Within the context of this invention a reactor is considered to be any confined zone in which the reaction between the aluminium source and magnesium source takes place. The reactor may be equipped with stirrers, baffles etcetera to ensure homogeneous mixing of the reactants. The reaction can take place with or without stirring, at ambient or at elevated temperature and at atmospheric or elevated pressure. Usually, a temperature between 0 and 100  
15 °C is used at or above atmospheric pressure. It is preferred to carry out the process at temperatures above 50 °C rather than at room temperature, because this results in anionic clays with sharper peaks in the x-ray diffraction pattern than anionic clays obtained at room temperature. The reactor may be heated by any heating source such as a furnace, microwave, infrared sources,  
20 heating jackets (either electrical or with a heating fluid), lamps, etcetera.

Said aqueous suspension in the reactor may be obtained by either feeding slurries of the starting materials, either combined or separate, to the reactor or adding magnesium source to a slurry of alumina trihydrate and/or its calcined  
25 form or vice versa and feeding the resulting slurry to the reactor. It is possible to treat, for instance the aluminium trihydrate slurry at elevated temperature and then add either the Mg source per se, or add the Mg source in a slurry or solution either to the reactor or the aluminium source slurry. Given particular facilities which might be available, the continuous process can be conducted  
30 hydrothermally. This is particularly advantageous, because it this is faster and a

higher conversion is obtained. There is no need to wash or filter the product, as unwanted ions (e.g. sodium, ammonium, chloride, sulphate) which are frequently encountered when using other preparation methods, are absent in the product.

- 5 In a further embodiment of the invention, the process is conducted in a multi-step process, e.g. a slurry of ATH and Mg source is treated thermally in a first reactor at a mild temperature, followed by a hydrothermal treatment in a second reactor. If desired a preformed anionic clay may be added to the reactor. Said preformed clay may be recycled anionic clay from the reaction mixture or  
10 anionic clay made separately by the process according to the invention or any other process.

- If desired, organic or inorganic acids and bases, for example for control of the pH, may be fed to the reactor or added to either the magnesium source or the  
15 aluminium source before they are fed to the reactor. An example of a preferred pH modifier is an ammonium base, because upon drying no deleterious cations remain in the anionic clay.

- If desired, the anionic clay prepared by the continuous process according to the  
20 invention may be subjected to ion exchange. Upon ion exchange the interlayer charge-balancing anions are replaced with other anions. Said other anions are the ones commonly present in anionic clays and include pillaring anions such as  $V_{10}O_{28}^{6-}$ ,  $Mo_7O_{24}^{6-}$ ,  $PW_{12}O_{40}^{3-}$ ,  $B(OH)_4^-$ ,  $B_4O_5(OH)_4^{2-}$ ,  $HBO_4^{2-}$ ,  $HGaO_3^{2-}$ ,  $CrO_4^{2-}$ . Examples of suitable pillaring anions are given in US 4774212 which is included  
25 by reference for this purpose. Said ion exchange can be conducted before or after drying the anionic clay formed in the slurry.

- The continuous process of the invention provides wide flexibility in preparing products with a wide range of Mg:Al ratios. The Mg:Al ratio can vary from 0.1 to  
30 10, preferably from 1 to 6, more preferred from 2 to 4, and especially preferred

to close to 3.

For some applications it is desirable to have additives, both metals and non-  
 metals, such as rare earth metals, Si, P, B, group VI, group VIII, alkaline earth  
 5 (for instance Ca and Ba) and/or transition metals (for example Mn, Fe, Ti, Zr,  
 Cu, Ni, Zn, Mo, Sn), present. Said metals and non-metals can easily be  
 deposited on the anionic clay or the solid solution according to the invention or  
 they can be added either to the alumina source or magnesium source which  
 are fed to the reactor or fed the reactor separately. Suitable sources of metals  
 10 or non-metals are oxides, halides or any other salt such as chlorides, nitrates  
 etcetera. In the case of a multi-step process the metals and non-metals may be  
 added in any of the steps. It can be especially advantageous for controlling the  
 distribution of the metals and non-metals in the anionic clay.

15 The present invention is illustrated by the following examples which are not to  
 be considered limitative by any means.

#### EXAMPLES

#### 20 COMPARATIVE EXAMPLES BASED ON THE STATE OF THE ART

##### Comparative Example 1

A commercially available sample of a Mg-Al carbonate anionic clay was  
 25 obtained from Reheis Chemical Company. Its PXRD pattern is shown for  
 illustration in Figure 1 -

D(A)	7.80	3.89	2.59
I/I <sub>0</sub>	100	40	35



Comparative Example 2

This comparative example illustrates the co-precipitation method where Mg and Al salt solutions are added to a solution of base. (US 3 979 523 Assignee  
5 Kyowa Chemical Industry, Japan)

A solution containing 0.04 M Of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and 0.08 M Of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in  
100 ml distilled water was added dropwise and with vigorous stirring to 150 ml  
of distilled water containing 0.05 M of  $\text{Na}_2\text{CO}_3$  at room temperature. Mg/Al ratio  
10 of 2.0. The pH was maintained close to 10 by the addition of 3N NAOH and the  
resulting slurry aged overnight at room temperature. The precipitate was  
separated by centrifuge, washed several times with hot distilled water then  
dried at 65 °C overnight.

15 The PXRD pattern obtained from this sample is shown in Figure 2. The results  
were:

D(A)	7.84	3.90	2.56
I/I <sub>0</sub>	100	40	20

Thermogravimetric analysis showed three weight losses: at approximately 100,  
20 250 and 450 °C which are ascribed to loss of physisorbed water, interlayer  
water and loss of  $\text{CO}_2$  and lattice dehydroxylation.

Comparative Example 3

The product obtained from Example 1 was calcined at 500 °C for 12 h. The product gave broad X-ray diffraction lines at 45 and 63 degrees two theta  
5 similar to those obtained for samples of calcined anionic clays prepared by other established methods with a Mg:Al ratio between 2 and 5.

Comparative Example 4

10 The product obtained from Example 2 was calcined at 500°C for 12 h. The product gave broad X-ray diffraction lines at 45 and 63 degrees two theta similar to those obtained for samples of calcined anionic clays prepared by other established methods with a Mg:Al ratio between 2 and 5.

15 Comparative Example 5

0.15 g of the product from Comparative Example 3 was added to 75 ml water at room temperature and stirred for 12 h. The product was filtered, washed and dried at 80 °C. The PXRD pattern indicated that the anionic clay structure had  
20 reformed with characteristic lines at 11.5, 23.5 and 35 ° in the PXRD.

Comparative Example 6

0. 15 g of the product from Example 4 was added to water at room temperature  
25 and stirred for 12 h. The product was filtered and dried at 80 °C. The PXRD pattern indicated that the product was similar to that for Comparative Example 5 and confirmed that the anionic clay structure had reformed.

## EXAMPLES OF THIS INVENTION

The anionic clays may be prepared under nitrogen or carbondioxide-free atmosphere, so that the anionic clay predominantly comprises hydroxide rather than predominantly carbonate as charge balancing anion. It is also possible to  
5 feed carbon dioxide to the reactor so that an anionic clay results with predominantly carbonate as charge balancing anion.

The following examples illustrate either the use of a Gibbsite (Micral 916 ®) obtained from J M Huber as a source of alumina or the use of BOC.  
10

Example 7

MgO in suspension and BOC with 5% of the product of Example 2 in  
15 suspension are fed to a reactor and hydrothermally treated at 170 °C. The resulting product was then dried in air at 65 °C overnight.

Example 8

20 MgO and Gibbsite in suspension are fed to a reactor and hydrothermally treated at 240 °C. The product was dried at 65 °C for 18 hours.

Example 9

25 Gibbsite is calcined in air at 400 °C for 2 hours. The calcined Gibbsite and MgO in suspension are fed to a reactor and treated hydrothermally at 200 °C. The product dried at 100 °C.

Example 10

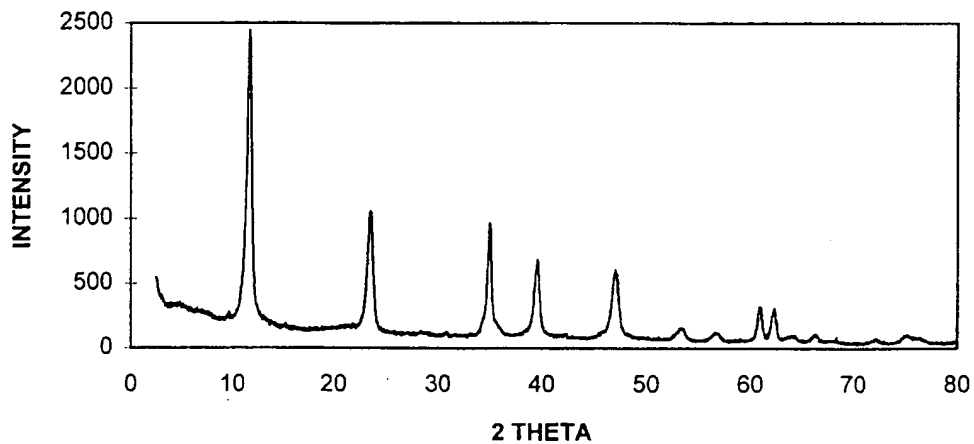
A sample of Gibbsite is calcined in air at 400 °C for 2 hours. The calcined gibbsite is then mixed with MgO in water. The pH of the mixture is adjusted to 6  
5 by the addition of HNO<sub>3</sub>, and fed to a reactor in which the mixture is treated hydrothermally at 200 °C. The product dried at 110 °C

We claim:

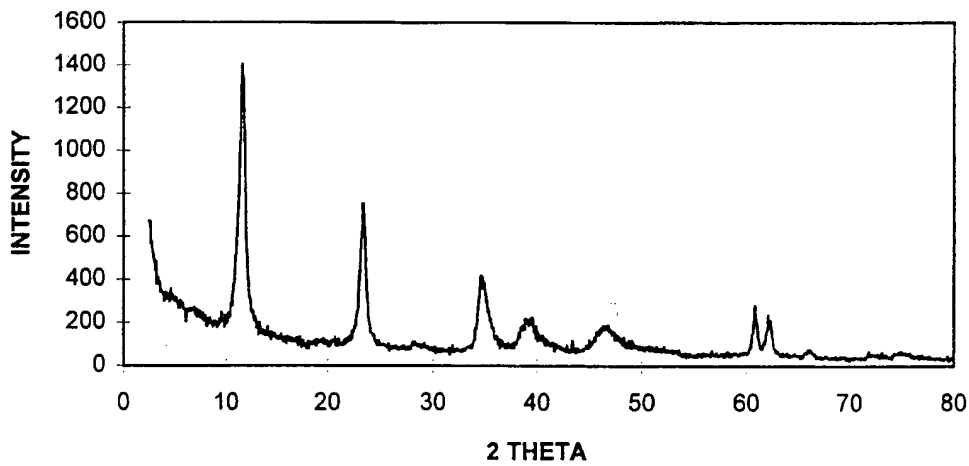
1. A continuous process for the preparation of anionic clays wherein an aluminium source and a magnesium source are fed to a reactor and reacted  
5 in aqueous suspension to obtain an anionic clay, the aluminium source being aluminium trihydrate and/or its thermally treated form.
2. A process according to claim 1 wherein the aluminium source is a thermally  
10 treated form of aluminium trihydrate.
3. A process according to claim 1 or 2 wherein the aluminium source is aluminium trihydrate.
4. A process according to any one of claims 1-3 wherein beside aluminium  
15 trihydrate and/or its thermally treated form other alumina sources are fed to the reactor.
5. A process according to any one of claims 1-4 wherein the aluminium source is fed to the reactor in the form of a slurry.
- 20 6. A process according to any one of claims 1-5 wherein the magnesium source is magnesium oxide and/or  $Mg(OH)_2$  and/or  $MgCO_3$ .
7. A process according to any one of the claims 1-6 wherein the magnesium  
25 source is fed to the reactor in the form of a slurry.
8. A process according to any one of claims 1-7 wherein the reaction takes place at a temperature between 0 and 100 °C at or above atmospheric  
30 pressure.

9. A process according to any one of claims 1-8 wherein the reaction takes place at a temperature above 50 °C at or above atmospheric pressure.
- 10.A process according to any one of claims 1-9 wherein the reaction is  
5 conducted at a temperature above 100 °C and increased pressure.
- 11.A process according to any one of claims 1-10 wherein metals or non-metals are fed to the reactor.
- 10 12.A process according to claim 11 wherein the metals or non-metals are added to an aluminium source slurry.
- 13.A process according to claim 11 wherein the metals or non-metals are added to a magnesium source slurry.  
15
- 14.A process according to any one of claims 1-11 wherein the anionic clay is subjected to an ion-exchange treatment.
- 15.A process according to any one of claims 1-12 wherein the anionic clay is  
20 ion exchanged with pillaring anions such as  $V_{10}O_{28}^{6-}$  and  $Mo_7O_{24}^{6-}$ .
- 16.A process according to any one of claims 1-13 wherein metals or non-metals are deposited on the anionic clay.
- 25 17.A process for the preparation of a Al-Mg-containing solid solution and/or spinel, wherein an anionic clay obtained by any one of the processes of claims 1-15 is subjected to a heat-treatment at a temperature between 300 and 1200 °C.

**FIGURE 1: X-RAY DIFFRACTION PATTERN FOR COMMERCIAL ANIONIC CLAY**



**FIGURE 2: X-RAY DIFFRACTION PATTERN FOR ANIONIC CLAY MADE BY CO-PRECIPITATION**



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 99/00858

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 C01F7/00

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 96 05140 A (HORN WILLIAM E JR ;CEDRO VITO III (US); MARTIN EDWARD S (US); STIN) 22 February 1996 cited in the application see the whole document	1-16
Y	---	17
X	DE 195 11 016 A (HENKEL KGAA) 26 September 1996 see the whole document	1-16
Y	---	17
X	EP 0 117 289 A (GIULINI CHEMIE) 5 September 1984 see the whole document	1-10
	---	
	-/--	

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

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Date of the actual completion of the international search

26 May 1999

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## INTERNATIONAL SEARCH REPORT

Int'l Application No

PCT/EP 99/00858

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 514 361 A (MARTIN EDWARD S ET AL) 7 May 1996 cited in the application see the whole document ---	1-4,6, 8-10
X	CAVANI F ET AL: "HYDROTALCITE-TYPE ANIONIC CLAYS: PREPARATION, PROPERTIES AND APPLICATIONS" CATALYSIS TODAY, vol. 11, no. 4, 1 January 1991, pages 173-291, XP000537043 cited in the application see page 211 - page 212	1,15
Y	p. 190, 197-198, 255-257 ---	17
X	EP 0 640 379 A (AIR PROD & CHEM) 1 March 1995 see claims 1-3,5 ---	17
X	DIMOTAKIS E D ET AL: "NEW ROUTE TO LAYERED DOUBLE HYDROXIDES INTERCALATED BY ORGANIC ANIONS: PRECURSORS TO POLYOXOMETALATE-PILLARED DERIVATIVES" INORGANIC CHEMISTRY, vol. 29, no. 13, 27 June 1990, page 2393/2394 XP000514229 p. 2394, scheme 1. see page 2163, column 1, line 37 - column 2, line 5 -----	17

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 99/00858

Patent document cited in search report	Publication date	Patent family member(s)	Publication date		
WO 9605140    A	22-02-1996	AU 704214 B	15-04-1999		
		AU 1559395 A	07-03-1996		
		BR 9508872 A	06-01-1998		
		CA 2197664 A	22-02-1996		
		EP 0776317 A	04-06-1997		
		HU 77873 A	28-09-1998		
		JP 10503465 T	31-03-1998		
		SK 21197 A	10-12-1997		
		US 5578286 A	26-11-1996		
		US 5728363 A	17-03-1998		
		US 5776424 A	07-07-1998		
		US 5728364 A	17-03-1998		
		US 5728365 A	17-03-1998		
US 5728366 A	17-03-1998				
US 5730951 A	24-03-1998				
DE 19511016    A	26-09-1996	WO 9630440 A	03-10-1996		
		EP 0817811 A	14-01-1998		
		JP 11502878 T	09-03-1999		
EP 0117289    A	05-09-1984	DE 3306822 A	30-08-1984		
		AT 35408 T	15-07-1988		
		CA 1217621 A	07-02-1987		
		DE 3377209 A	04-08-1988		
		JP 1059977 B	20-12-1989		
		JP 1573376 C	20-08-1990		
		JP 59182227 A	17-10-1984		
		US 4539195 A	03-09-1985		
US 5514361    A	07-05-1996	AU 1559495 A	29-11-1995		
		BR 9507557 A	05-08-1997		
		CA 2189020 A	09-11-1995		
		CZ 9603162 A	16-04-1997		
		EP 0759888 A	05-03-1997		
		HU 75979 A	28-05-1997		
		JP 9512519 T	16-12-1997		
		SK 139596 A	06-08-1997		
		WO 9529874 A	09-11-1995		
		US 5578286 A	26-11-1996		
		US 5728363 A	17-03-1998		
		US 5776424 A	07-07-1998		
		US 5728364 A	17-03-1998		
		US 5728365 A	17-03-1998		
		US 5728366 A	17-03-1998		
		US 5730951 A	24-03-1998		
EP 0640379    A	01-03-1995	US 5407652 A	18-04-1995		
		BR 9403333 A	20-06-1995		
		CA 2130589 A	28-02-1995		
		DE 69409450 D	14-05-1998		
		DE 69409450 T	27-08-1998		
		JP 2637049 B	06-08-1997		
		JP 7163870 A	27-06-1995		
		KR 142375 B	01-06-1998		
		SG 48048 A	17-04-1998		
		US 5472677 A	05-12-1995		